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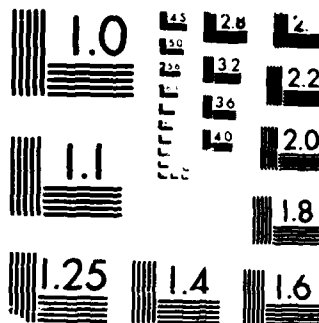
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FINAL REPORT

CONTRACT N00014-86-0480^K

BY

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DEPARTMENT OF MACROMOLECULAR SCIENCE

CASE WESTERN RESERVE UNIVERSITY

FEBRUARY 10, 1988

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I

1. We have worked on nitrile terminated aliphatic diacetylene dimers. This study was initially focused on the diacetylenic dimer of undecynonitrile: $\text{HC}=\text{C}(\text{CH}_2)_8\text{CN}$ (in order to save space and time, the shorthand notation "8 nitrile dimer" was adopted. The 8 nitrile dimer is the nitrile analog to the dimer of 1,11-dodecadiyne which was shown by us to undergo a topochemical crosspolymerization reaction to yield a semiconducting organic polymer. In order to overcome some difficulties in obtaining large single crystals, we began to investigate the polar nitrile terminator which may undergo solid state polymerization.

The synthesis of the dimer of undecynonitrile is illustrated in Figure 1. The final product was purified by liquid chromatography and is believed to be very pure. Single crystals and polycrystalline mats of the nitrile dimer (MP = 13°C) were irradiated at various subambient temperatures. Upon spectroscopic investigation of these samples it was determined that only the diacetylene moiety polymerized to any extent upon exposure to various combinations of UV and gamma radiation. An effort was made to use electrochemical methods to effect the polymerization of both functional groups in the 8 nitrile dimer but no evidence was found to support this. A two step approach was attempted whereby the diacetylene groups would be polymerized by radiation and then the nitrile group polymerization would be initiated by thermal

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means in a manner analogous to the cyclization of polyacrylonitrile. As the temperature approached 200°C, it was found that the aliphatic chains terminated by nitrile groups on the semi-polymerized dimer were flexible enough to allow large-scale movement and thereby forbid the polymerization of nitriles.

We investigated the reactivity of nitrile dimers with fewer methylene groups in the side chains. The 5 nitrile monomer was obtained commercially and dimerized. Its polymerizability, however, was similar to that of the 8 nitrile dimer. Synthetic work was subsequently focused on the 0-, 1-, 2- and 3-nitrile dimers. The 0 nitrile material was obtained using the route outlined in Figure 2a. As a completely rigid 8 atom molecule it is too rigid to allow the nitrile polymerization to occur as determined by molecular models. The synthesis of the 1 nitrile dimer has been met with many difficulties. Various approaches have been attempted (Figures 2b-2e); however, each of these have failed for a particular reason. Although not yet completed, the pathway shown in Figure 2f appears to be successful and can be used on the 2- and 3-nitrile dimers. It is hoped that these materials will have enough local flexibility to allow the propagation of the activated nitrile center while maintaining the proper amount of rigidity needed to obey the least motion principle as applied to polymerization.

We are finishing a determination of the crystal structures of the 8 nitrile dimer and the polymerized product so that we can understand the molecular mechanism of that solid state reaction.

II

Work has primarily involved the characterization of the previously synthesized α,ω -alkyldiyne dimers and their respective solid state polymerized polymers. Dimers of the structure $[\text{HC}=\text{C}(\text{CH}_2)_n\text{C}=\text{C}]_2$ where $n=3,4,5,6,7,8$ were synthesized via a controlled Glaser oxidative coupling and subsequent high vacuum fractional distillation. All compounds with the exception of the $n=3$ dimer exhibited gamma, UV, and thermally induced solid state polymerization. The resultant polymers (below T_m of the corresponding monomer) are highly colored blue polymers. Current work has focused on the characterization of these polymers with respect to: reactivity of the terminal acetylenes in the solid state, thermal transitions in the polydiacetylene backbone, and the thermochromic and solvatochromic behavior of the bulk polymers as well as polymer solutions.

Fourier transform infrared spectroscopy (FTIR) studies show that although the diacetylene rod readily polymerizes, the terminal acetylene moieties fail to appreciably convert to polymer. Thin crystalline films of dimers exposed to UV radiation (254 nm 800 uW/cm² @ 5 cm) show no loss in the acetylenic hydrogen absorbance (3300 cm⁻¹ and 630 cm⁻¹) after exposure times of greater than 45 minutes. Bulk samples crystallized ($\Delta T = 10^\circ\text{C}$) and exposed to 1 Mrad, 5 Mrad, and 10 Mrad of ⁶⁰Co gamma radiation were able to be dissolved in hot benzene. FTIR

spectra of thin polymer films formed by evaporation of these solutions on KBr windows also showed no loss of the acetylinic hydrogen absorbances.

Thermal studies (DSC) show that ^{60}Co gamma radiation polymerized samples (polymerized above 25%) exhibit an endothermic transition above the crystalline melt temperature (T_m of the monomer) characteristic of melting. The transition temperature of the polymer seems to be dependent upon the number of pendant methylene spacers, or simply stated the length of the substituent groups on the polydiacetylene backbone, increasing with increasing length. As in the unpolymerized dimers, evidence also suggests that an odd-even effect exists. The difference in the transition temperature between n and $n-1$ polymerized dimers is significantly greater than between n and $n+1$ dimers when n is even.

Visual studies of bulk polymerized dimers (via UV and gamma radiation) heated above their respective polymer melt temperatures showed a reversible thermochromic transition from red to yellow and back to red upon cooling. Originally blue material heated through T_m of the monomer undergoes the expected blue to red transition as the melted residual monomer solvates the polymer chain. UV/Visible spectroscopy studies have shown the color change to be the result of an absorbance maxima shift from 650 nm to 540 nm. It is felt the shift is due to a disordering and relaxation of the pendant side groups causing a loss of coordinated conjugation in the polydiacetylene main chain. Preliminary X-ray diffractometry studies show a loss of several scattering peaks as the material goes from the blue form to the red form.

The reversible chromic transition between the red form and the yellow form was found to be the result of an absorbance maxima shift from 540 nm to 480 nm. Unlike the blue to red transition, the red to yellow transition appears to be fully reversible. Upon heating from the red material to the yellow material and cooling back the red one sees an increase and narrowing of the absorbance maxima at 540 nm indicative of a reordering of fringe material to a more homogeneous conjugation length. Although this is consistent with a melt reordering phenomena, preliminary x-ray diffraction studies show the red form and the reordered red form to have extremely poor crystallinity, and thus should not be considered a melt recrystallization behavior.

UV/Visible spectroscopy studies have shown that the polymerized dimers also exhibit a reversible red to yellow transition in solution. Polymer samples dissolved in a good solvent (i.e. benzene) have an absorbance maxima of 455 nm and are a vibrant yellow color. Upon the addition of a miscible nonsolvent (i.e. ethanol), one sees a gradual red shifting of the 455 nm maxima of up to 30 nm and the rise of a shoulder that develops into a well defined peak at 530 nm. Although there are small (5 nm) variations in these maxima between dimers, all exhibit the same behavior irrespective of polymer concentration. Large variations occur between polymerized dimers with respect to the mole fraction of nonsolvent that must be added in order to induce the chromic transition. This is most likely due to differences in the length of the pendant side groups as well as the difference in degrees of polymerization (i.e. polymer chain length) between the dimers.

Reversibility can be achieved by the addition of more solvent, or by heating. If the red solution is heated to force the yellow transition, the red transition will reoccur as the solution cools. The addition of a large amount of nonsolvent will cause the eventual precipitation of the red polymer. This work is being considered for erasable memory storage and may be patented.

III

Three poly(alkyldiyne) macromonomers have been synthesized and characterized: poly(1,6-heptadiyne) (Pl6H), poly(1,8-nonadiyne) (Pl8N), and poly(1,11-dodecadiyne) (Pl11D). Thermochromic and solvatochromic transitions have been discovered and characterized in the crosspolymerized forms of these systems. The discovery of chromic transitions in these systems is significant in that it was initially presumed that chromic behavior would be prevented by the network structure formed upon crosspolymerization.

Synthesis

The monomers 1,6-heptadiyne and 1,8-nonadiyne are commercially available. The 1,11-dodecadiyne had to be synthesized, and we have used an established method from the literature for this purpose. The macromonomer synthesis used is based on a catalytic Glaser coupling in the literature, but has been optimized to maximize purity and molecular weight. The polymers obtained are white, thermoplastic materials with good film-forming and mechanical properties. All three polymers can be crosspolymerized using UV and gamma radiation to produce highly colored materials. These materials will also slowly crosspolymerize in the dark at room temperature.

Thermal Analysis

A thermal analysis study of poly(1,8-nonadiyne) was performed to determine if an autocatalytic crosspolymerization could be induced. It was found that crosspolymerization could not be thermally accelerated to a measurable degree. During the course of this study, we noted a unique melting behavior in P18N which was observed upon repeated thermal cycling. Initially it appeared that the behavior was due to thermal crosspolymerization, but the behavior was shown to be related to the peculiar nucleation behavior of the material. Thermal analysis was also shown to be useful as a qualitative measure of the degree of crosspolymerization in UV irradiated materials.

Crosspolymerization

All three macromonomers synthesized will undergo radiation induced crosspolymerization. Qualitative information has been obtained for the UV induced crosspolymerization reaction of P18N using UV-VIS and resonance Raman spectroscopies. These studies indicate that as conversion increases, the average conjugation length decreases.

Preliminary experiments with P111D suggest that this material can be formed in two crystal modifications. The first modification is

observed when films are cast from methylene chloride solution. The material crosspolymerizes slowly at room temperature in the dark and takes many hours before any color is developed in the material. The second modification is formed in films cast from chloroform solutions. Blue color is observed after less than 10 minutes at room temperature in the dark. A determination of the structural differences between these two forms is now underway.

Chromic Behavior

Solvatochromism. It has been found that when the crosspolymerized macromonomers are immersed into certain solvents a chromic transition can be induced, even though the crosspolymerized materials are insoluble. The chromic change is more severe at low degrees of crosspolymerization (i.e. the largest optical shift is seen at low conversions) and has been shown to be irreversible. This behavior has been investigated using UV-VIS spectroscopy.

Thermochromism. Although the crosspolymerized macromonomers are infusible, thermochromic transitions have been induced in these materials. All of the macromonomers investigated demonstrate this behavior, but Pl8N has been the most thoroughly investigated material. When the crosspolymerized material is heated above the melting point of the macromonomer, a distinct color change takes place in the material. This change persists even after returning the material to room

temperature. Again, the lower the conversion, the more distinct the chromic change. Visual examination of the material during heating shows that the chromic change at elevated temperature is more severe than after the material is returned to room temperature. This behavior is currently being quantified with in-situ heating studies using UV-VIS and resonance Raman spectroscopies.

The conversion dependence of the chromic behavior has allowed us to determine that the solid state reaction is homogeneous (as opposed to heterogeneous, as are some solid state reactions). Resonance Raman studies (using 6328A light) have shown that the crosspolymerization reaction in the highly ordered regions of the sample is complete after about 6m of UV exposure. The regions of the sample where shorter conjugation lengths are formed (i.e. the less perfect regions) are currently being investigated using resonance Raman (with an argon ion laser).

Mechanochromism. It has been observed that when the macromonomers are brought to a low degree of conversion and then stretched, the material will undergo a chromic transition from blue to yellow. This behavior is likely due to destruction of the crystalline regions upon deformation of the sample.

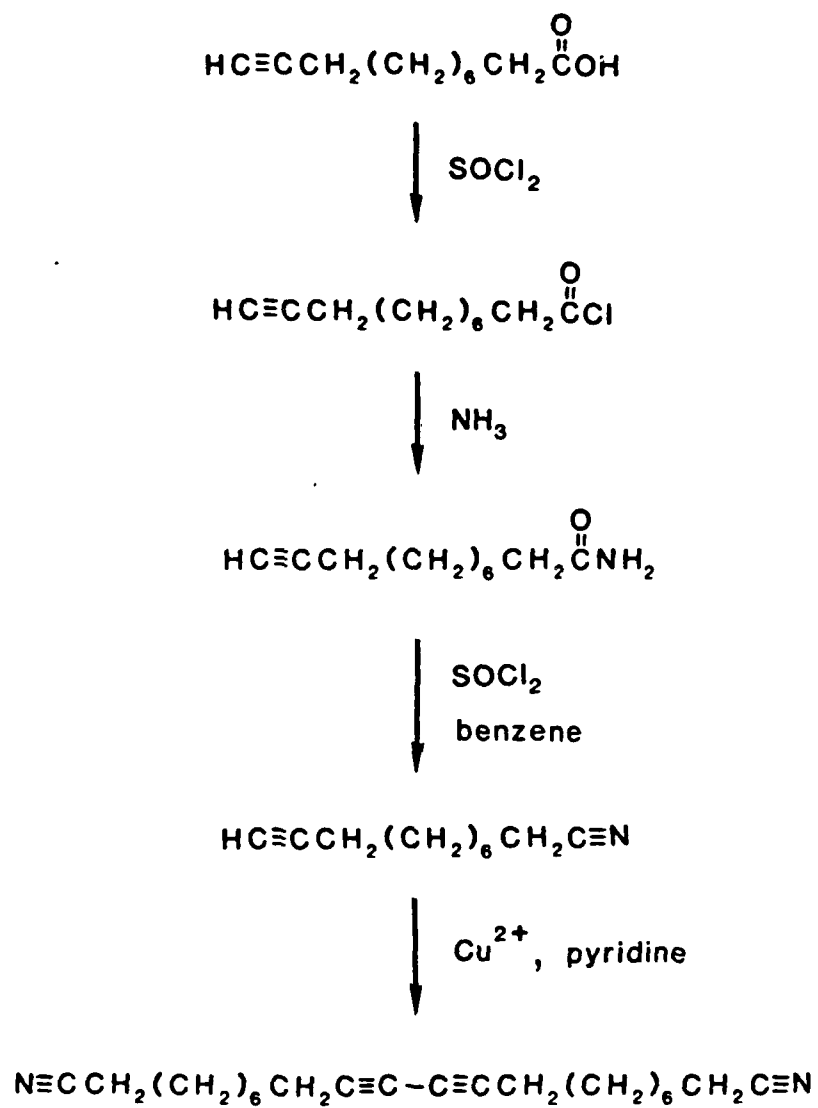


FIGURE 1

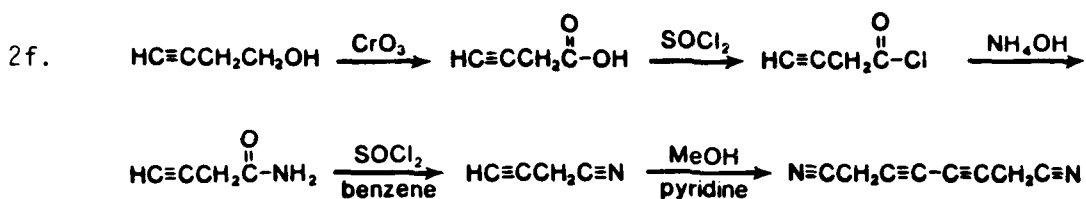
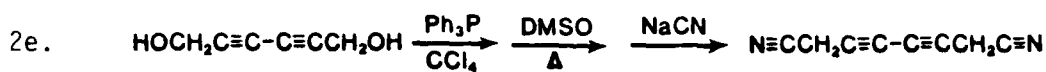
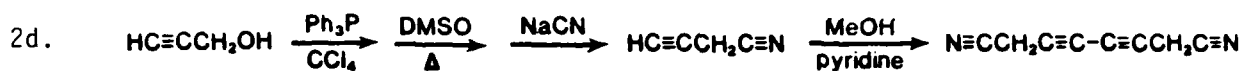
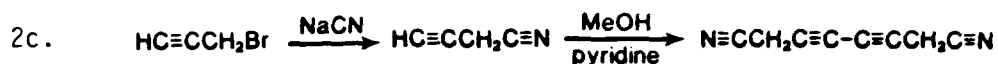
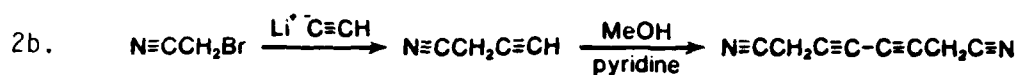
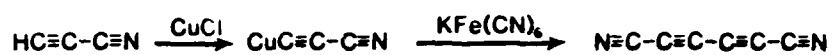
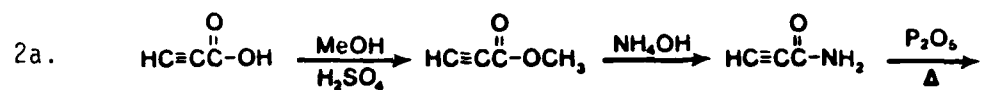


FIGURE 2

Index of Publications

1. "Conduction in Polymerized Polyfunctional Diacetylenes," R.P. Grasso, M.K. Thakur, J.B. Lando, Mol. Cryst. Liq. Cryst., 118, 377 (1985).
2. "Structural Studies of Novel Polydiyne Materials," R.J. Butera, R.P. Grasso, M.K. Thakur, J.B. Lando, A.C.S. Symposium Series 337, (1987).
3. "Conversion and Chromic Behavior of Crosspolymerized Poly(1,8-nonadiyne)," R.J. Butera, J.B. Lando, B. Simic-Glavoeski, Macromolecules, 20, 1722 (1987).
4. "Analytical Form of the Electron Diffraction Scattering Factors for Common Atoms," R.P. Grasso, J.B. Lando, Jour. Mater. Sci. Lett., in press.
5. "Melting Behavior of Poly(1,8-nonadiyne) Macromonomer," R.J. Butera, J.B. Lando, in preparation.
6. "Solid State Reactivity of Several Poly(α,ω -alkyldiyne) Macromonomers," R.J. Butera, J.B. Lando, in preparation.
7. "Chromic Transitions in Cross-Polymerized Poly(α,ω -alkyldiyne) Macromonomers," R.J. Butera, J.B. Lando, in preparation.

8. "Chromic Behavior of Poly(diacetylenes): A Review," R.J. Butera,
J.B. Lando, in preparation.

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